



Crystal structure of *catena*-poly[[diaqua-cadmium(II)]- μ -3,3'-(1,3-phenylene)-diacrylate]

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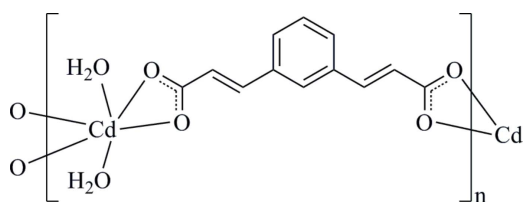
In the crystal of the title polymeric complex, $[\text{Cd}(\text{C}_{12}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2]_n$, the Cd^{II} cation, located on a twofold rotation axis, is coordinated by two water molecules and chelated by two phenylenediacylate anions (mpda) in a distorted octahedral geometry. The mpda anions bridge the Cd^{II} cations, forming helical chains propagating along the c -axis direction. The mpba anion has twofold symmetry with two benzene C atoms located on the twofold rotation axis. In the crystal, $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link the polymeric helical chains into a three-dimensional supramolecular architecture.

Keywords: V-shaped ligand; helical chain; chiral coordination polymer; cadmium; crystal structure.

CCDC reference: 1054223

1. Related literature

For V-shaped metal complexes coordinated by the phenylenediacylate anion, see: Liu *et al.* (2013). For related metal-organic coordination polymers with an *m*-phenylenedi-carboxylate ligand, see: Yang *et al.* (2014).



2. Experimental

2.1. Crystal data

$[\text{Cd}(\text{C}_{12}\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2]$

$M_r = 364.62$

Orthorhombic, $C222_1$
 $a = 5.3145$ (12) Å
 $b = 11.991$ (3) Å
 $c = 19.767$ (5) Å
 $V = 1259.7$ (5) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.75$ mm⁻¹
 $T = 293$ K
 $0.35 \times 0.32 \times 0.25$ mm

2.2. Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
 $T_{\text{min}} = 0.59$, $T_{\text{max}} = 0.68$

3205 measured reflections
1107 independent reflections
950 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.155$
 $S = 1.08$
1107 reflections
96 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.93$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.64$ e Å⁻³
Absolute structure: Flack (1983), 1035 Friedel pairs
Absolute structure parameter: 0.07 (19)

Table 1
Selected bond lengths (Å).

Cd1—O1	2.329 (6)	Cd1—O3W	2.199 (7)
Cd1—O2	2.380 (6)		

Table 2
Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3W}-\text{H1A}\cdots\text{O1}^{\text{i}}$	0.85 (2)	1.88 (4)	2.695 (9)	160 (8)
$\text{O3W}-\text{H1B}\cdots\text{O2}^{\text{ii}}$	0.84 (2)	1.92 (3)	2.736 (8)	162 (8)

Symmetry codes: (i) $x - 1, -y + 2, -z + 2$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5838).

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supporting information

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Crystal structure of *catena*-poly[[diaquacadmium(II)]- μ -3,3'-(1,3-phenylene)diacrylato]

Xiao-Ping Zhang, Xin Chen and Kun-Lin Huang

S1. Introduction

In crystal engineering, a great interest is focused on the supramolecular self-assembly of helical or chiral coordination polymers from appropriately bridging ligands and metallic tectons through either coordinate bonds and hydrogen bonds. Although much effort has been devoted to the assembly of helical or chiral coordination polymers based on chiral or achiral ligands, the design and construction of chiral coordination polymer based on helical topology is still a great challenge for chemists.

S2. Experimental

All reagents and solvents employed were commercially available and were used as received without further purification.

S2.1. Synthesis and crystallization

A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (62 mg, 0.25 mmol), *m*-phenylenediacrylic acid (H_2mpda , 44 mg, 0.2 mmol) and H_2O (10 mL) was sealed in a 25 mL stainless steel reactor with a Teflon liner, heated to 413 K for 3 d and then cooled to room temperature. The crystals were washed with methanol to give the title complex in about 35% yield (based on the H_2mpda ligand).

S2.2. Refinement

All non-hydrogen atoms are easily found from the different Fourier maps and refined anisotropically. All H atoms of H_2O molecules are found in the difference Fourier map. The C-bound H atoms of aromatic rings were refined using a riding model [0.93 Å (CH) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

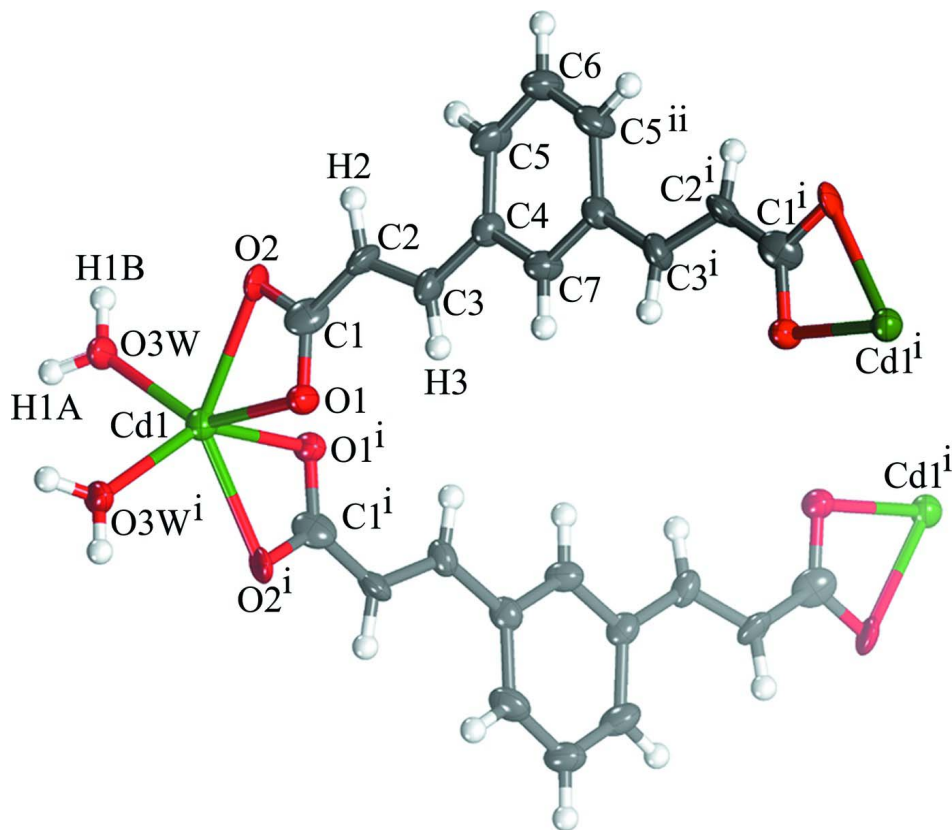
S3. Results and discussion

The *m*-phenylenediacrylate (*mpda*) has various conformations for the rotation of carbon-carbon bonds, such as the C—C single bonds between aromatic rings and C=C bonds. The V-shaped *mpda* coordinated with metal ions have been documented (Liu *et al.*, 2013). But the *mpda* has not been well exploited in constructing metal-organic coordination polymers in comparison with the *m*-phenylenedicarboxylate ligand (Yang *et al.*, 2014). Herein, we report a poly[(*m*-phenylenediacrylate)(water)cadmium] with the formulae $[\text{Cd}(\text{mpda})(\text{H}_2\text{O})_2]_n$ (**1**). The title compound crystallizes in the chiral $C222$ (1) space group, and contains a homochiral left-handed single-stranded helical chain.

In the structure of **1** (Fig. 1), the Cd^{2+} centre adopts a six-coordinated mode with a distorted octahedral geometry (CdO_6) *via* binding to two water O atoms and four O atoms from two different CO_2^- groups of *mpda* ligands [O1, O2, O1ⁱ, O2ⁱ; symmetry code: (i) $x, -y+2, -z+2$]. The Cd—O distances range from 2.199 (7) to 2.380 (6) Å. Taking account of the O3W—Cd1—O3Wⁱ angle of 92.1 (4)°, the coordination mode of Cd^{2+} ion may play an determining role in the formation of the Cd1ⁱ...Cd1...Cd1ⁱ angle of 85.65°. Each *mpda* ligand with a monodentate mode bridges two different Cd^{2+} ions, *via*

carboxylate groups at each end of the ligand molecule. Of the structure of the mpda, two acrylate groups ($\text{CH}=\text{CH}-\text{COO}^-$) are located at the benzene ring in a *trans*-position fashion. The dihedral angles of the $\text{CH}=\text{CH}-\text{COO}^-$ and $\text{C}_6\text{H}_4-\text{CH}=\text{CH}$ group are *ca.* 11.4° and 7.9° , respectively, while that of $\text{C}1\cdots\text{C}7\cdots\text{C}6\cdots\text{C}1^i$ is 180° . These dihedral angle data indicate that the mpda ligand is nearly coplanar and there exist intramolecular $\pi-\pi$ electronic conjugations.

The mpda ligands serve as V-shaped bridges to link the metal ions into infinite helical coordination chains running along the *c*-axis, with the $\text{Cd}\cdots\text{Cd}$ distance separated by mpda being 14.54 \AA . The helical pitch of $19.767(5) \text{ \AA}$ is equal to the *c* dimension of the unit cell. There has the one and only left-handed single-stranded chain in **1**, which reveals that this work presents a new unusual example of homochiral architecture based on the helical topology. In **1**, the packing of the helical chains is sustained by complicated hydrogen bonds and $\pi-\pi$ stacking involving all the coordinated water molecules, and the $\text{C}=\text{C}$ double bonds and phenylene rings of the mpda ligands. Each phenylene ring from one chain interacts with a $\text{C}=\text{C}$ double bond from another chain, with the interplane distances being 3.53 \AA . Careful examination of the structure indicates that strong interchain hydrogen bonds of $\text{O}3\text{W}-\text{H}1\text{A}\cdots\text{O}1^{\text{iii}}$ [$2.695(6) \text{ \AA}$; Symmetry code: (iii) $x-1, -y+2, -z+2$] exist between the two independent chains. It is clear that the hydrogen ($\text{H}1\text{A}$) atoms of one coordinated water molecule serve as the acceptors, while the oxygen ($\text{O}1^{\text{iii}}$) atoms of the mpda ligands serve as the donors in each self-recognition site. The above-mentioned $\pi-\pi$ and $\text{O}3\text{W}-\text{H}1\text{A}\cdots\text{O}1^{\text{iii}}$ interactions bring the helical coordination chains into wave-shaped two-dimensional layers. Further a three-dimensional supramolecular architecture is result from wave-shaped motifs through the interlayer hydrogen bonds of $\text{O}3\text{W}-\text{H}1\text{B}\cdots\text{O}2^{\text{iv}}$ [$2.736(8) \text{ \AA}$; Symmetry code: (iv) $x-1/2, -y+3/2, -z+2$].

**Figure 1**

Part of the crystal structure of the mpda ligand and Cd^{II} centres in **(1)**, showing the atom-numbering scheme.

Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $x, -y + 2, -z + 2$; (ii) $-x + 2, y, -z + 3/2$].

catena-Poly[[diaquacadmium(II)]- μ -3,3'-(1,3-phenylene)diacrylate]

Crystal data

[Cd(C₁₂H₈O₄)(H₂O)₂]

$M_r = 364.62$

Orthorhombic, C222₁

Hall symbol: C 2c 2

$a = 5.3145$ (12) Å

$b = 11.991$ (3) Å

$c = 19.767$ (5) Å

$V = 1259.7$ (5) Å³

$Z = 4$

$F(000) = 720$

$D_x = 1.922$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1107 reflections

$\theta = 2.0$ – 25.0°

$\mu = 1.75$ mm⁻¹

$T = 293$ K

Block, colorless

$0.35 \times 0.32 \times 0.25$ mm

Data collection

Bruker SMART APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2008)

$T_{\min} = 0.59, T_{\max} = 0.68$

3205 measured reflections

1107 independent reflections

950 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 25.0^\circ, \theta_{\min} = 2.1^\circ$

$h = -5 \rightarrow 6$

$k = -13 \rightarrow 14$

$l = -19 \rightarrow 23$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.039$ $wR(F^2) = 0.155$ $S = 1.08$

1107 reflections

96 parameters

2 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sitesH atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 7.5572P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.93 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.64 \text{ e } \text{\AA}^{-3}$ Absolute structure: Flack (1983), 1035 Friedel
pairs

Absolute structure parameter: 0.07 (19)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	-0.00336 (16)	1.0000	1.0000	0.0311 (3)
O1	0.2947 (11)	0.9898 (5)	0.9139 (3)	0.0332 (13)
O2	0.1598 (11)	0.8310 (5)	0.9546 (3)	0.0335 (14)
O3W	-0.2906 (13)	0.8960 (5)	1.0493 (4)	0.0438 (18)
C1	0.307 (2)	0.8841 (8)	0.9156 (4)	0.040 (2)
C2	0.4734 (19)	0.8224 (7)	0.8726 (5)	0.039 (2)
H2	0.4462	0.7460	0.8689	0.046*
C3	0.6643 (18)	0.8655 (8)	0.8375 (4)	0.0329 (19)
H3	0.6894	0.9420	0.8411	0.040*
C4	0.8387 (19)	0.8040 (7)	0.7936 (4)	0.0297 (19)
C5	0.848 (2)	0.6888 (8)	0.7930 (5)	0.041 (2)
H5	0.7472	0.6494	0.8231	0.049*
C6	1.0000	0.6307 (10)	0.7500	0.042 (3)
H6	1.0000	0.5531	0.7500	0.050*
C7	1.0000	0.8616 (10)	0.7500	0.033 (3)
H7	1.0000	0.9392	0.7500	0.039*
H1A	-0.436 (7)	0.917 (7)	1.062 (4)	0.02 (2)*
H1B	-0.288 (15)	0.826 (2)	1.056 (4)	0.01 (2)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.0265 (5)	0.0292 (5)	0.0377 (5)	0.000	0.000	-0.0032 (3)

O1	0.029 (3)	0.024 (3)	0.046 (3)	-0.001 (3)	0.007 (3)	-0.001 (3)
O2	0.012 (3)	0.027 (3)	0.062 (4)	-0.006 (3)	0.013 (3)	-0.004 (3)
O3W	0.024 (4)	0.028 (3)	0.079 (5)	-0.002 (3)	0.015 (4)	0.001 (4)
C1	0.053 (6)	0.040 (5)	0.027 (4)	-0.009 (5)	0.000 (5)	-0.009 (4)
C2	0.031 (5)	0.026 (4)	0.059 (6)	-0.015 (5)	0.006 (5)	-0.007 (4)
C3	0.024 (4)	0.037 (5)	0.038 (5)	-0.008 (4)	0.005 (4)	-0.001 (4)
C4	0.030 (4)	0.031 (5)	0.028 (4)	-0.004 (5)	0.004 (4)	0.002 (3)
C5	0.046 (6)	0.030 (5)	0.046 (5)	-0.012 (5)	0.008 (5)	0.004 (4)
C6	0.048 (8)	0.024 (6)	0.054 (7)	0.000	0.008 (8)	0.000
C7	0.041 (7)	0.025 (6)	0.032 (6)	0.000	0.006 (7)	0.000

Geometric parameters (Å, °)

Cd1—O1 ⁱ	2.329 (6)	C2—C3	1.334 (13)
Cd1—O1	2.329 (6)	C2—H2	0.9300
Cd1—O2 ⁱ	2.380 (6)	C3—C4	1.468 (12)
Cd1—O2	2.380 (6)	C3—H3	0.9300
Cd1—O3W	2.199 (7)	C4—C5	1.383 (14)
Cd1—O3W ⁱ	2.199 (7)	C4—C7	1.398 (10)
Cd1—C1 ⁱ	2.727 (10)	C5—C6	1.363 (12)
O1—C1	1.270 (12)	C5—H5	0.9300
O2—C1	1.269 (12)	C6—C5 ⁱⁱ	1.363 (12)
O3W—H1A	0.85 (2)	C6—H6	0.9300
O3W—H1B	0.84 (2)	C7—C4 ⁱⁱ	1.398 (10)
C1—C2	1.432 (14)	C7—H7	0.9300
O3W—Cd1—O3W ⁱ	92.1 (4)	Cd1—O3W—H1B	128 (6)
O3W—Cd1—O1 ⁱ	100.3 (3)	H1A—O3W—H1B	105 (9)
O3W ⁱ —Cd1—O1 ⁱ	140.0 (2)	O2—C1—O1	119.0 (9)
O3W—Cd1—O1	140.0 (2)	O2—C1—C2	118.8 (9)
O3W ⁱ —Cd1—O1	100.3 (3)	O1—C1—C2	122.1 (9)
O1 ⁱ —Cd1—O1	94.3 (3)	C3—C2—C1	125.3 (9)
O3W—Cd1—O2 ⁱ	124.6 (3)	C3—C2—H2	117.3
O3W ⁱ —Cd1—O2 ⁱ	86.4 (2)	C1—C2—H2	117.3
O1 ⁱ —Cd1—O2 ⁱ	55.3 (2)	C2—C3—C4	126.4 (8)
O1—Cd1—O2 ⁱ	94.2 (2)	C2—C3—H3	116.8
O3W—Cd1—O2	86.4 (2)	C4—C3—H3	116.8
O3W ⁱ —Cd1—O2	124.6 (3)	C5—C4—C7	117.8 (9)
O1 ⁱ —Cd1—O2	94.2 (2)	C5—C4—C3	122.0 (9)
O1—Cd1—O2	55.3 (2)	C7—C4—C3	120.2 (8)
O2 ⁱ —Cd1—O2	137.3 (3)	C6—C5—C4	122.6 (10)
O3W—Cd1—C1 ⁱ	116.0 (3)	C6—C5—H5	118.7
O3W ⁱ —Cd1—C1 ⁱ	113.7 (3)	C4—C5—H5	118.7
O1 ⁱ —Cd1—C1 ⁱ	27.7 (3)	C5—C6—C5 ⁱⁱ	118.5 (12)
O1—Cd1—C1 ⁱ	93.6 (3)	C5—C6—H6	120.7
O2 ⁱ —Cd1—C1 ⁱ	27.7 (3)	C5 ⁱⁱ —C6—H6	120.7
O2—Cd1—C1 ⁱ	116.4 (3)	C4 ⁱⁱ —C7—C4	120.8 (11)
C1—O1—Cd1	93.9 (6)	C4 ⁱⁱ —C7—H7	119.6

C1—O2—Cd1	91.5 (5)	C4—C7—H7	119.6
Cd1—O3W—H1A	127 (6)		

Symmetry codes: (i) $x, -y+2, -z+2$; (ii) $-x+2, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3W—H1A \cdots O1 ⁱⁱⁱ	0.85 (2)	1.88 (4)	2.695 (9)	160 (8)
O3W—H1B \cdots O2 ^{iv}	0.84 (2)	1.92 (3)	2.736 (8)	162 (8)

Symmetry codes: (iii) $x-1, -y+2, -z+2$; (iv) $x-1/2, -y+3/2, -z+2$.